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KINETICS OF THERMOCHEMICAL GAS-SOLID REACTIONS IMPORTANT IN THE VENUS SULFUR CYCLE

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  - Fegley (1988b) "Cosmochemical Trends of Volatile Elements in the Solar System" invited chapter in *Workshop on the Origins of Solar Systems* ed. J.A. Nuth and P. Sylvester, LPI Technical Report No. 88-04.
  - Prinn & Fegley (1988) "Solar Nebula Chemistry: Origin of Planetary, Satellite, and Cometary Volatiles," invited chapter in *Planetary and Satellite Atmospheres: Origin and Evolution* (University of Arizona Press, Tucson), in press for 1988.

1. INTRODUCTION

This report is the final report for **NASA** Grant **NAGW-821** entitled "Kinetics of Thermochemical Gas-Solid Reactions Important in the Venus Sulfur Cycle". This report covers the grant period of 11/01/85 - 10/31/88.

The major accomplishments achieved during this grant period are described in section (2a) of this report and in the enclosed reprints and preprints.

2. FINAL REPORT

(a) Accomplishments

The thermochemical net reaction

$$CaCO_3 \text{ (calcite)} + SO_2(g) \rightarrow CaSO_4 \text{ (anhydrite)} + CO(g) \quad (1)$$

is predicted to be an important sink for incorporation of SO_2 into the Venus crust (Prinn 1985a, b, c; Fegley 1988; Fegley and Prinn 1988). Furthermore, several authors have noted that the CO_2 partial pressure at the Venus surface ($P_{CO_2} \sim 92$ bars) is almost identical to the equilibrium CO_2 pressure ($P_{CO_2} \sim 102$ bars) developed at the Venus surface temperature of 737 K from the Urey equilibrium

$$CaCO_3 \text{ (calcite)} + SiO_2 \text{ (quartz)} = CaSiO_3 \text{ (wollastonite)} + CO_2(g) \quad (2)$$

and have proposed that this equilibrium is buffering the CO_2 pressure in the Venus atmosphere (e.g., Urey 1959; Mueller 1964; Lewis 1970; Vinogradov and Volkov 1971). These predictions concerning possible roles for calcite on Venus, the exemplary nature of reaction (1), and the availability of high purity $CaCO_3$ in several forms led us to study reaction (1) as a paradigm for SO_2 removal on Venus.

Our philosophy in studying this reaction was to establish the reaction rate law and to understand the dependence of rate on experimental variables such as temperature, SO_2 partial pressure, CO_2 partial pressure, and O_2 partial pressure. We can then extrapolate the experimental results to conditions of pressure, temperature, and composition relevant to the surface of Venus. However, our objective was not to attempt a precise simulation of the Venus surface conditions. For example, although the SO_2 molecular number density at the surface of Venus was reproduced in our experiments, the CO_2 molecular number density (i.e., total pressure) was not. Instead, an inert dilutant gas (Ar) was used to study the variation of the rate with the CO_2 partial pressure.

Our experimental approach was a variant of the thermogravimetric method employed by materials scientists to study the kinetics of many thermochemical gas-solid reactions (e.g., Beruto and Searcy 1974; Bratton and Brindley 1965; Gordon and Kingery 1967; Powell and Searcy 1978; Turkdogan 1968; Turkdogan *et al.*, 1965). The principal difference was that we heated different samples for varying time periods along isotherms instead of continuously monitoring the weight change of a single sample as a function of time. Our method was preferable in this case because of the slow reaction rate (days to weeks) and because it allows us to use powerful microscopic techniques such as scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS/SEM) to examine the surface chemical and morphological changes as the reaction proceeds. Results of these techniques will be discussed and illustrated later.

Clear calcite crystals (Iceland spar) were heated at constant temperature in SO_2-bearing gas streams for varying time periods. The gas-solid reaction apparatus, which is schematically illustrated in Figure A1 of the Appendix, was used to do this. The purity of the calcite crystals was checked by chemical analysis using inductively coupled plasma emission spectroscopy (ICP). The analytical results, which are given in Table A1 of the Appendix, show that total impurities are $\sim$ 350 ppm by mass with Mg ($\sim$ 200 ppm) being the major impurity. X-ray diffraction was also used to check the calcite crystals. These results (Table A2) show that all the observed X-ray lines match the literature values for calcite.

Before heating, the calcite crystals were carefully weighed using a Mettler analytical balance with a 0.01 milligram sensitivity. Their geometric dimensions were measured to the nearest 0.00025 cm (0.0001 inch) with a micrometer. These measurements are necessary to calculate the surface areas of the samples because we are interested in measuring rates per unit area. The micrometer measurements were checked by comparing the observed sample weights with the geometrically calculated weight. These values generally agreed within ± 5%. Also, replicate weight and sample size measurements were made to calculate 1 σ uncertainties via standard methods of small number statistics (Shoemaker *et al.*, 1974).

The experiments were done at ambient atmospheric pressures with analyzed $SO_2 - CO_2$ gas mixtures nominally containing 1% (by volume) SO_2. These mixtures were chosen so that the SO_2 molecular number density in the laboratory experiments is about the same as at the surface of Venus where the atmospheric pressure is about 100 times larger (Seiff 1983) but the SO_2 volume mixing ratio is about 100 times smaller (von Zahn *et al.*, 1983). As Table A3 shows, the mixtures also typically contained < 1 ppm O_2 and ≤ 30 ppm H_2O as impurities. Standard flow meters were used to monitor and control gas flow during the experiments. A microprocessor controlled vertical tube furnace (Deltech model DT-31-RS-OS) was used in all experiments. Separate thermocouples were used to control the furnace ($Pt_{94}Rh_6$ vs. $Pt_{70}Rh_{30}$) and to monitor the sample temperature (Pt vs. $Pt_{90}Rh_{10}$). The sample thermocouple was calibrated at the melting points of Au and Ag prior to use and was placed a few mm away from the samples in the constant temperature zone ($\sim$ 40 mm long) of the furnace. The combined uncertainties in temperature control and measurement are less than ± 5°C. At the end of an experimental run, samples were quenched in the furnace by simultaneously shutting off the power and switching from the $SO_2 - CO_2$ gas mixture to pure CO_2. (A CO_2 pressure of 1 atmosphere will prevent calcite dissociation at temperatures less than 1175 K, which were used in our experiments.) There are several good reasons for using this quenching procedure: (a) the slow rate of reaction leads to negligible reaction during the $\sim$ 10 minutes required to flush the furnace tube with pure CO_2, (b) the initial cooling rate of 25-30°C per minute, depending on the run temperature, and the strong dependence of rate on temperature also leads to negligible reaction during the $\sim$ 3-4 minutes required to cool the sample by 100°C. We note that for our highest temperature run used to determine the activation energy for reaction (1), any additional reaction during the first 4 minutes of cooling, when substantial amounts of the reactant gas are still in the furnace tube, is less than 0.04% of the total number of SO_2 molecules reacted during the entire run (see experimental conditions for R43 in Table A5).

The rate of reaction (1) was determined by three independent methods: (a) reweighing the reacted samples and measuring the weight gain at the end of reaction, (b) using SEM to measure the porosity and thickness of the reacted surface layers from micrographs of external and fracture surfaces, and (c) chemical analyses by ion chromatography of the amounts of SO_4^{2-} in the reacted samples.

SEM examination of many samples (in combination with X-ray line scans and EDS/SEM) showed that $CaSO_4$ layers covered all external surfaces of the reacted calcite crystals. The X-ray line scan across the fracture surface of a reacted sample (Figure A2) and the fracture surface micrograph of another reacted sample (Figure A3) are representative of the results obtained. X-ray diffraction patterns of reacted calcite crystals and of more extensively reacted $CaCO_3$ synthetic powders showed only lines due to anhydrite and to unreacted calcite. This is illustrated in Table A4 which shows that all (non-calcite) lines in the product are due to anhydrite. Both the literature values for anhydrite and our separate results for a natural anhydrite sample from the MIT mineral collection agree with the values for the product.

The experimental rate data and run conditions for the subset of runs used to determine the activation energy for reaction (1) are summarized in Table A5 and Figure A4. (Other experimental runs were either preliminary runs, runs used to derive the rate dependence on other experimental variables, or were runs on other calcium minerals.) **These rate data are the first experimental measurements of the rate of any chemical weathering reaction postulated to occur on the surface of Venus.** The use of these data in estimating the present-day rate of volcanism on Venus will now be described.

A weighted linear least squares fit to all the rate data in Table A5 gives the equation for the rate $R = 10^{19.64(\pm 0.28)}\ exp\ (-15,248(\pm 2970)/T)$ molecules cm^{-2} sec^{-1}. As illustrated in Figure A4, the corresponding activation energy is 126.8 ± 5.4 kJ/mole. The rate of reaction (1) was extrapolated downward to Venus surface temperatures (~ 660 – 750 K) using this equation, the Pioneer Venus radar altimetry data (Masursky *et al.*, 1980), and the Pioneer Venus atmospheric (P, T) profile (Seiff, 1983) to take the altitude dependence of the rate into account.

The results of these calculations are displayed in Figure A5, which illustrates several important points. First, because the rate of reaction (1) exponentially decreases with decreasing temperature, the reaction of SO_2 with calcite on the Venus surface will be slower at higher elevations (and thus lower temperatures) than it will be at lower elevations (and thus higher temperatures). Second, assuming that calcite is uniformly distributed over the Venus surface, most of the global anhydrite formation via reaction (1) will take place at and around the median planetary radius of 6051.5 km. This is simply a consequence of the unimodal surface topography distribution on Venus. Third, summing up the reaction rates in all elevation increments (see Fig. A5) gives a derived global mean SO_2 reaction rate $\sim 4.6 \times 10^{10}$ molecules cm^{-2} s^{-1}. Based on the median planetary radius of 6051.5 km (Masursky *et al.*, 1980), this corresponds to a SO_2 reaction rate of $\sim 2.1 \times 10^{29}$ SO_2 molecules s^{-1} over the entire Venus surface.

Chemical analyses of the Venus surface by the Venera 13, 14 and Vega 2 spacecraft (Surkov *et al.*, 1984, 1986) gave a CaO content (by mass) of 7.90% (weighted mean). Assuming that our experimentally determined rate is representative of the SO_2 depletion rate from the Venus atmosphere via reaction with calcium minerals on the Venus surface, the observed SO_2 column density of 2.2×10^{23} molecules cm^{-2} (von Zahn *et al.*, 1983) would be removed from the Venus atmosphere in $\sim 1.9 \times 10^6$ years in the absence of a comparable sulfur source. This is a geologically short time period. However, unless the observed H_2SO_4 clouds, which are formed by the sunlight-powered conversion of SO_2 into H_2SO_4 cloud particles (Esposito *et al.*, 1983), are equally short-lived, their maintenance requires a comparable sulfur source.

This source must be endogenic because the flux of sulfur provided by infalling cosmic material is too small to balance the sulfur flux into the Venus crust. The calculated SO_2 removal rate over the entire surface of Venus is equivalent to $\sim 2.8 \times 10^{13}$ grams of sulfur per year. However, the measured terrestrial flux of infalling material, which is roughly applicable to Venus because of the similar sizes and masses of the two planets, is only $\sim 7.8 \times 10^{10}$ grams per year (Kyte and Wasson 1986), and only contributes at most $\sim 4.6 \times 10^9$ grams sulfur per year assuming the most sulfur-rich $C1$ chondrite composition (Mason 1971).

The most plausible endogenic sulfur source is volcanism, which has occurred on Venus in the past (Basilevsky and Head 1988), and which may also have led to the increased SO_2 levels above the Venus cloud tops that were observed by the Pioneer Venus orbiter (Esposito 1984; Esposito *et al.*, 1988). The rate of volcanism required to balance the atmospheric SO_2 depletion (via reactions with calcium minerals on the Venus surface) depends on the sulfur content of the erupted material (both gas and magma). If this material has an overall S/Si mass ratio of 0.03, the weighted mean of the Venera 13, 14 and Vega 2 surface analyses (Surkov *et al.*, 1984, 1986), the corresponding rate of volcanism is ~ 1 km^3 yr^{-1}. (This model as well as the other two models below assumes a rock density of 3 g cm^{-3}.) Figure A6 illustrates that this is about 20 times smaller than the terrestrial value.

Two other plausible models for the S/Si ratio of the erupted material on Venus are also shown in Figure A6. The first model assumes that the bulk S/Si ratio of the erupted material is ~ 0.1, as in ordinary chondrites (Mason, 1971). The corresponding volcanism rate is ~ 0.4 km^3 yr^{-1}. The second model assumes that the S/Si ratio of the erupted material is ~ 0.004, as in the Earth's crust (Ronov and Yaroshevsky 1976) and gives a volcanism rate of ~ 11 km^3 yr^{-1}. Thus, three plausible models for the bulk S/Si ratio of the erupted material give volcanism rates ranging from ~ 0.4 to ~ 11 km^3 yr^{-1}, a range that is smaller than the terrestrial rate of ~ 20 km^3 yr^{-1}.

All three rates will scale as ϵ^{-1}, where ϵ is the S degassing efficiency ($0 < \epsilon \leq 1$) of the erupted material. This efficiency is probably close to unity because sulfur gases will be expelled directly into the atmosphere and the hot, sulfur-bearing magmas will rapidly react with and lose S to the atmosphere, both during the eruption and later during cooling. An example of the facile nature of these S degassing reactions is provided by our preliminary experiments on pyrite (FeS_2) weathering. Figure A7 shows pyrite crystals on a natural dolomite ($CaMg(CO_3)_2$) crystal prior to any high temperature reaction. However, as Figures A8 and A9 show, heating at ~ 980°C for only 3 hours is sufficient to degas the sulfur from the pyrite crystals and convert them to iron oxides. Reactions at typical magmatic temperatures of ~ 1100-1200°C will be even faster and sulfur degassing will also be even more thermodynamically favorable.

Figure A6 also illustrates the two widely discordant volcanism rates that have been estimated by geophysical methods. Solomon and Head (1982) and Turcotte (1988) have both estimated volcanism rates in the range of ~ 200-300 km^3 yr^{-1} by scaling terrestrial heat production to Venus and then assuming that volcanism is the sole heat transport mechanism. However, Grimm and Solomon (1987) have estimated a much lower limit of less than 2 km^3 yr^{-1} for the Venus volcanism rate by an analysis of the areal density of impact craters on the Venera 15, 16 radar images.

The geochemically derived volcanism rate, which is based on our experimental study of the SO_2 + calcite reaction, is independent of these two discordant rates. In fact, the geochemically derived rate can in principal be used to test if either (or neither) of the geophysically derived rates is correct. Finally, our work also suggests that Venus is less volcanically active than the Earth.

(b) Publication Record

The following refereed papers supported by **NASA** Grant **NAGW-821** during the 3-year period 11/01/85 - 10/31/88 have been published or are in press:

(1) R.G. Prinn and B. Fegley, Jr. "The Atmospheres of Venus, Earth, and Mars: A Critical Comparison," invited chapter in *Ann. Rev. Earth Planet. Sci.*, 15, 171-212 (1987).

(2) R.G. Prinn and B. Fegley, Jr. "Solar Nebula Chemistry: Origin of Planetary, Satellite, and

Cometary Volatiles," invited chapter in *Planetary and Satellite Atmospheres; Origin and Evolution* (University of Arizona Press, Tucson), in press for 1988.

(3) B. Fegley, Jr. "Cosmochemical Trends of Volatiles in the Solar System," invited chapter in *Workshop on the Origins of Solar Systems* ed. J.A. Nuth and P. Sylvester, LPI Technical Report No. 88-04.

The following manuscripts supported by **NASA** Grant **NAGW-821** have been submitted for publication or are in preparation:

(4) B. Fegley, Jr. and R.G. Prinn "The Rate of Volcanism on Venus,," submitted to *Nature*.

(5) B. Fegley, Jr. "The Rate of Chemical Weathering on the Surface of Venus: Experimental Study of Anhydrite Formation," in preparation for the H. Wänke Festschrift volume of *Z. Naturfor.*

Also, the following papers based on research supported by **NASA** Grant **NAGW-821** were delivered at scientific meetings (speaker underlined) during the past year:

(6) B. Fegley, Jr. "First Laboratory Measurements of Thermochemical Kinetics of SO_2 Reactions with Putative Venus Crustal Minerals," 19th Annual Division of Planetary Sciences of AAS meeting, Pasadena, CA, 10-13 November 1987. Abstract: *Bull. Am. Astron. Soc.*, **19**, 871.

(7) B. Fegley, Jr. "Thermochemical Kinetics of SO_2 Reactions with Possible Venus Crustal Minerals: First Data for Calcite," 19th Lunar and Planetary Science Conference, Houston, TX, 14-18 March 1988, Abstract: *Lunar Planet. Sci.*, **XIX**, 315-316.

(8) B. Fegley, Jr. "First Laboratory Data on the Rates of Sulfur Gas-Mineral Interactions Relevant to Venus," Brown University-Vernadsky Institute Microsymposium 7, Providence, RI, 21-23 March 1988.

(9) B. Fegley, Jr. "The Rate of Chemical Weathering on the Surface of Venus: Experimental Study of Anhydrite Formation," scheduled to be presented at the Wänke Festschrift Conference, Max-Planck-Institut für Chemie, Mainz, W. Germany, 5-6 September 1988.

In addition, the PI was invited to contribute a report based on research supported by **NASA** Grant **NAGW-821** to the 1988 Planetary Geosciences Annual Report. This is the first time this report, which is intended to publicize the research results in Planetary Geosciences, has been prepared. Approximately 40 PI's were invited to contribute.

(c) Students Involved in Research

The following MIT undergraduate students participated in research supported by **NASA** Grant **NAGW-821**. The student's contributions to specific publications from section 2b are listed in parenthesis after the student's name.

(1) M. Camitta (assisted in building gas-solid reaction apparatus)

(2) A. Petropoulos (paper 4)

(3) S. Rowell (paper 4)

(4) B. Vanderlaan (paper 2)

6. REFERENCES

Allen, J.M. and Fawcett, J.J. (1982) *J. Petrol.*, **23**, 215-239.

Anders, E. (1986) in *Comet Nucleus Sample Return*, ESA SP-249, pp. 31-39.

Asaki, J., Mori, S., Ikeda, M., and Kondo, Y. (1985) *Met. Trans.*, **16B**, 627-638.

Barber, D.J. (1985) *Clay Minerals*, **20**, 415-454.

Basilevsky, A.T. and Head, J.W. (1988) *Ann. Rev. Earth Planet. Sci.*, **16**, 295-317.

Bernatowicz, T., Fraundorf, G., Ming, T., Anders, E., Wopenka, B., Zinner, E., and Fraundorf, P. (1987) *Nature*, **330**, 728-730.

Berner, R.A. and Holdren, G.R., Jr. (1977) *Geology*, **5**, 369-372.

Beruto, D. and Searcy, A.W. (1974) *J. Chem. Soc. Faraday Trans. I* **70**, 2145-2153.

Bratton, R.J. and Brindley, G.W. (1965) *Trans. Faraday Soc.*, **61**, 1017-1025.

Bunch, T.E. and Chang, S. (1980) *Geochim. Cosmochim. Acta*, **44**, 1543-1577.

Carroll, D. (1970) *Rock Weathering*, Plenum Press, NY.

Chou, L. and Wollast, R. (1984) *Geochim. Cosmochim. Acta* **48**, 2205-2217.

Costello, J.A. and Tressler, R.E. (1986) *J. Amer. Ceram. Soc.*, **69**, 674-681.

Donahue, T.M. (1988) "Comets and Water on Venus: Venus was Wet," preprint.

DuFresne, E.R. and Anders, E. (1962) *Geochim. Cosmochim. Acta*, **26**, 1085-1114.

Esposito, L.W. (1984) *Science*, **223**, 1072-1074.

Esposito, L.W., Knollenberg, R.G., Marov, M.Ya., Toon, O.B., and Turco, R.P. (1983) in *Venus* eds. D.M. Hunten, L. Colin, T.M. Donahue, and V.I. Moroz, University of Arizona Press, Tucson, pp. 474-564.

Esposito, L.W. Copley, M., Eckert, R., Gates, L., Stewart, A.I.F., and Worden, H. (1988) *J. Geophys. Res.*, **93**, 5267-5276.

Fegley, B., Jr. (1988) in *Workshop on the Origins of Solar Systems* ed. J.A. Nuth and P. Sylvester, LPI Technical Report No. 88-04, pp. 51-60.

Fegley, B., Jr. and Barringer, E.A. (1984) in *Better Ceramics Through Chemistry*, ed. C.J. Brinker, D.E. Clark, and D.R. Ulrich, North-Holland, NY, pp. 187-197.

Fegley, B., Jr. and Prinn, R.G. (1988) "The Rate of Volcanism on Venus", submitted to *Nature*.

Ferry, J.M. (1983) *J. Petrol.*, **24**, 343-376.

Gokarn, A.N. and Doraiswamy, L.K. (1971) *Chem. Eng. Sci.*, **26**, 1521-1533.

Gordon, R.S. and Kingery, W.D. (1967). *J. Amer. Ceram. Soc.*, **50**, 8-14.

Greenwood, H.J. (1963) *J. Petrol.*, **4**, 317-351.

Greenwood, H.J. (1967) *Amer. Mineral.*, **52**, 1669-1680.

Grimm, R.E. and Solomon, S.C. (1987) *Geophys. Res. Let.*, **14**, 538-541.

Grossman, L. (1972) *Geochim. Cosmochim. Acta*, **36**, 597-619.

Hashimoto, A. and Grossman, L. (1987) *Geochim. Cosmochim. Acta*, **51**, 1685-1704.

Helgeson, H.C. (1971) *Geochim. Cosmochim. Acta*, **35**, 421-469.

Hills, A.W.D. (1968) *Chem. Eng. Sci.*, **23**, 297-320.

Holdren, G.R., Jr. and Speyer, P.M. (1985) *Geochim. Cosmochim. Acta*, **49**, 675-681.

Hua, X., Adam, J., Palme, H., and El Goresy, E.A. (1988) *Geochim. Cosmochim. Acta*, **52**, 1389-1408.

Hulbert, S.F. (1969) *Brit. Ceram. Soc. J.*, **6**, 11-20.

Hyatt, E.P., Cutler, I.B., and Wadsworth, M.E. (1958) *J. Amer. Ceram. Soc.*, **41**, 70-74.

Ingraham, T.R. and Marier, P. (1963) *Canad. J. Chem. Eng.*, **41**, 170-173.

Knauss, K.G. and Wolery, T.J. (1986) *Geochim. Cosmochim. Acta*, **50**, 2481-2497.

Kyte, F.T. and Wasson, J.T. (1986) *Science*, **232**, 1225-1229.

Larimer, J.W. (1967) *Geochim. Cosmochim. Acta*, **31**, 1215-1238.

Larimer, J.W. (1975) *Geochim. Cosmochim. Acta*, **39**, 389-392.

Larimer, J.W. and Anders, E. (1967) *Geochim. Cosmochim. Acta*, **31**, 1239-1270.

Larimer, J.W. and Bartholomay, M. (1979) *Chim. Geochim. Cosmochim. Acta*, **43**, 1455-1466.

Lewis, J.S. (1970) *Earth Planet. Sci. Lett.*, **10**, 73-80.

Lewis, J.S. (1972) *Earth Planet. Sci. Lett.*, **15**, 286-290.

Lewis, J.S. and Prinn, R.G. (1984) *Planets and Their Atmospheres Origin and Evolution*, Academic Press, NY.

Loughnan, F.C. (1969) *Chemical Weathering of the Silicate Minerals*, Elsevier, NY.

Lynch, D.C. and Elliott, J.F. (1978) *Met. Trans*, **9B**, 691-704.

Lynch, D.C. and Elliott, J.F. (1980) *Met. Trans*, **11B**, 415-425.

Mason, B. ed. (1971) *Handbook of Elemental Abundances in Meteorites*, Gordon and Breach, NY.

Masursky, H., Eliason, E., Ford, P.G., McGill, G.E., Pettengill, G.H., Schaber, G.G., and Schubert, G.J. (1980) *J. Geophys. Res.*, **85**, 8232-8260.

Ming, T. and Anders, E. (1988) *Geochim. Cosmochim. Acta*, **52**, 1235-1244.

Mueller, R.F. (1964) *Icarus*, **3**, 285-298.

Mueller, R.F. and Saxena, S.K. (1977) *Chemical Petrology*, Springer-Verlag, NY.

Nagahara, H. (1984) *Geochim. Cosmochim. Acta*, **48**, 2581-2595.

Nelson, R., Nuth, J.A., and Donn, B. (1987) *Proc. Lunar Planet. Sci. Conf. 17th J. Geophys. Res.*, **92**, E657-E662.

Nuth, J.A., Donn, B., Deseife, R., Donn, A., and Nelson, R. (1986) *Proc. Lunar Planet. Sci. Conf. 16th J. Geophys. Res.*, **91**, D533-D537.

Powell, E.K. and Searcy, A.W. (1978) *J. Amer. Ceram. Soc.*, **61**, 216-221.

Prinn, R.G. (1985a) in *Recent Advances in Planetary Meteorology* ed. G.E. Hunt, Cambridge University Press, London, pp. 1-15.

Prinn, R.G. (1985b) in *The Photochemistry of Atmospheres* ed. J.S. Levine, Academic Press, NY, pp. 281-336.

Prinn, R.G. (1985c) in *Scientific American*, **252**, 46-53.

Prinn, R.G. and Fegley, B., Jr. (1987) *Ann. Rev. Earth Planet. Sci.*, **15**, 171-212.

Prinn, R.G. and Fegley, B., Jr. (1988) "Solar Nebula Chemistry: Origin of Planetary, Satellite, and Cometary Volatiles," in *Planetary and Satellite Atmospheres: Origin and Evolution* ed. S. Atreya, J. Pollack, and M.S. Matthews, University of Arizona Press, Tucson, in press for 1988.

Rimstidt, J.D. and Dove, P.M. (1986) *Geochim. Cosmochim. Acta*, **50**, 2509-2516.

Ronov, A.B. and Yaroshevsky, A.A. (1976) *Geochem. Intl.*, **13**, 89-121.

Rubin, A., Fegley, B., Jr. and Brett, R. (1988) in *Meteorites and the Early Solar System* ed. J. Kerridge and M.S. Matthews, University of Arizona Press, Tucson, in press for 1988.

Satterfield, C.N. and Feakes, F. (1959) *A.I.Ch.E.J.*, **5**, 115-122.

Schairer, J.F. (1959) in *Physiochemical Measurements at High Temperatures* ed. J.O. Bockris, Butterworths, London, pp. 117-134.

Schlichting, J. (1979a) *Ber. Dt. Keram. Ges.*, **56**, 196-200.

Schlichting, J. (1979b) *Ber. Dt. Keram. Ges.*, **56**, 256-261.

Schott, J., Berner, R.A. and Sjöberg, E.L. (1981) *Geochim. Cosmochim. Acta*, **45**, 2123-2135.

Seiff, A. (1983) in *Venus* ed. D.M. Hunten, L. Colin, T.M. Donahue, and V.I. Moroz, University of Arizona Press, Tucson, pp. 215-279.

Shoemaker, D.P., Garland, C.W. and Steinfeld, J.I. (1974) *Experiments in Physical Chemistry*, McGraw Hill, NY, p. 34.

Sohn, H.Y. and Won, S. (1985) *Met. Trans.*, **16B**, 645-661.

Solomon, S.C. and Head J.W. (1982) *J. Geophys. Res.*, **87**, 9236-9246.

Surkov, Yu. A., Barsukov, V.L., Moskalyova, L.P., Kharyukova, V.P. and Kemurdzhian, A.L. (1984) *Proc. Lunar Planet. Sci. Conf. 14th J. Geophys Res.*, **89**, B393-B402.

Surkov, Yu. A., Moskalyova, L.P., Kharyukova, V.P. Dudins, A.D., Smirnov, G.G., and Zaitseva, S. Ye. (1986) *Proc. Lunar Planet. Sci. Conf. 17th J. Geophys Res.*, **91**, E215-E218.

Szekely, J., Evans, J.W., and Sohn, H.Y. (1976) *Gas-Solid Reactions*, Academic Press, NY.

Tanner, S.B., Kerrick, D.M., and Lasaga, A.C. (1985) *Amer. J. Sci.*, **285**, 577-620.

Turcotte, D.L. (1988) *Lunar Planet. Sci.*, **XIX**, 1206-1207.

Turkdogan, E.T. (1968) *Trans. AIME*, **242**, 1665-1672.

Turkdogan, E.T., McKewan, W.M., and Zwell, L. (1965) *J. Phys. Chem.*, **69**, 327-334.

Urey, H.C. (1952) *The Planets*, Yale University Press, New Haven.

Urey, H.C. (1959) in *Handbuch der Physik*, vol. 52, Springer-Verlag, Berlin, pp. 363-418.

Vinogradov, A.P. and Volkov, V.P. (1971) *Geochim. Intl.*, **8**, 463-467.

von Zahn, U., Kumar, S., Niemann, H., and Prinn, R.G. (1983) in *Venus* ed. D.M. Hunten, L. Colin, T.M. Donahue, and V.I. Moroz, University of Arizona Press, Tucson, pp. 299-430.

Wegner, W.W. and Ernst, W.G. (1983) *Amer. J. Sci.*, **283A**, 151-180.

Worrell, W.L. and Turkdogan, E.T. (1968) *Trans. AIME*, **242**, 1673-1678.

Zinner, E., Ming, T., and Anders, E. (1987) *Nature*. **330**, 730-732.

TABLE A1

Impurities in Calcite Crystals (ICP Analyses)[†]

Impurity Level (ppm by mass)

Element	Sample 1	Sample 2
Al	6.48	6.92
Mg	220	212
Mn	24.3	22.1
Si	12.4	11.8
Sr	72.2	69.8
Zr[‡]	23.6	26.2
TOTAL IMPURITIES	359	349

[†] Inductively Coupled Plasma Emission Spectroscopy

[‡] The Zr impurity probably comes from the ZrO_2 grinding media used to pulverize the crystals for chemical analysis.

TABLE A2

X-Ray Diffraction Results

Calcite

d-Values

Reactant	Literature
3.025	3.035
2.485	2.495
2.280	2.285
2.089	2.095
1.905	1.913
1.872	1.875

TABLE A3

Analyses of $SO_2 - CO_2$ Gas Mixtures[a]

RUN	% SO_2	ppm O_2	ppm H_2O
R36[b]	1.06	< 1	21
R43[b]	1.06	< 1	21
R44[b]	1.06	< 1	21
R45[c]	1.08	< 1	34
R50[d]	0.96	< 1	11
R51[d]	0.96	< 1	11

[a] Only the runs used to determine the activation energy of reaction (1) are listed.

[b] The same tank was used in these runs and the impurity analyses were done when the tank was nearly empty.

[c] The impurity analyses were done when the tank was nearly empty.

[d] The same tank was used in these runs.

TABLE A4

X-Ray Diffraction Results

Anhydrite

d-Values

Product	Anhydrite	Literature
3.484	3.479	3.498
2.835	2.837	2.849
2.318	2.320	2.328
2.198	2.203	2.208
2.173		2.183
1.985		1.993
1.742	1.745	1.749
1.643	1.643	1.648

- All lines in product can be attributed to anhydrite or unreacted calcite
- 23 hour exposure on product, 12 hour exposure on natural anhydrite

TABLE A5

Rate Data Used to Calculate the Activation Energy

Sample	$T(^\circ C)^a$	Duration (Hours)	Rate $\times 10^{-12}$ (molecules cm^{-2} s^{-1})^b
R44-1	602	95	1.67 ± 0.19^c
R45-1	602	314	0.85 ± 0.77
			1.05 ± 0.12^c
R45-3	602	314	1.01 ± 0.11^c
R45-4	602	314	1.20 ± 0.51
			0.68 ± 0.48^d
R36-1	746	96	8.43 ± 2.93
			13.6 ± 6.0^d
R36-2	746	96	23.2 ± 6.2
			19.9 ± 11.0^d
R50-1	747	192	9.19 ± 1.60
R50-3	747	192	10.5 ± 7.8
R51-1	748	96	13.2 ± 4.0
R51-2	748	96	10.3 ± 5.6
R43-1	848	91	60.4 ± 6.8
			57.1 ± 31.7^d
R43-2	848	91	53.2 ± 7.0
			67.2 ± 43.4^d
R43-3	848	91	58.1 ± 7.0
			48.4 ± 12.1^d

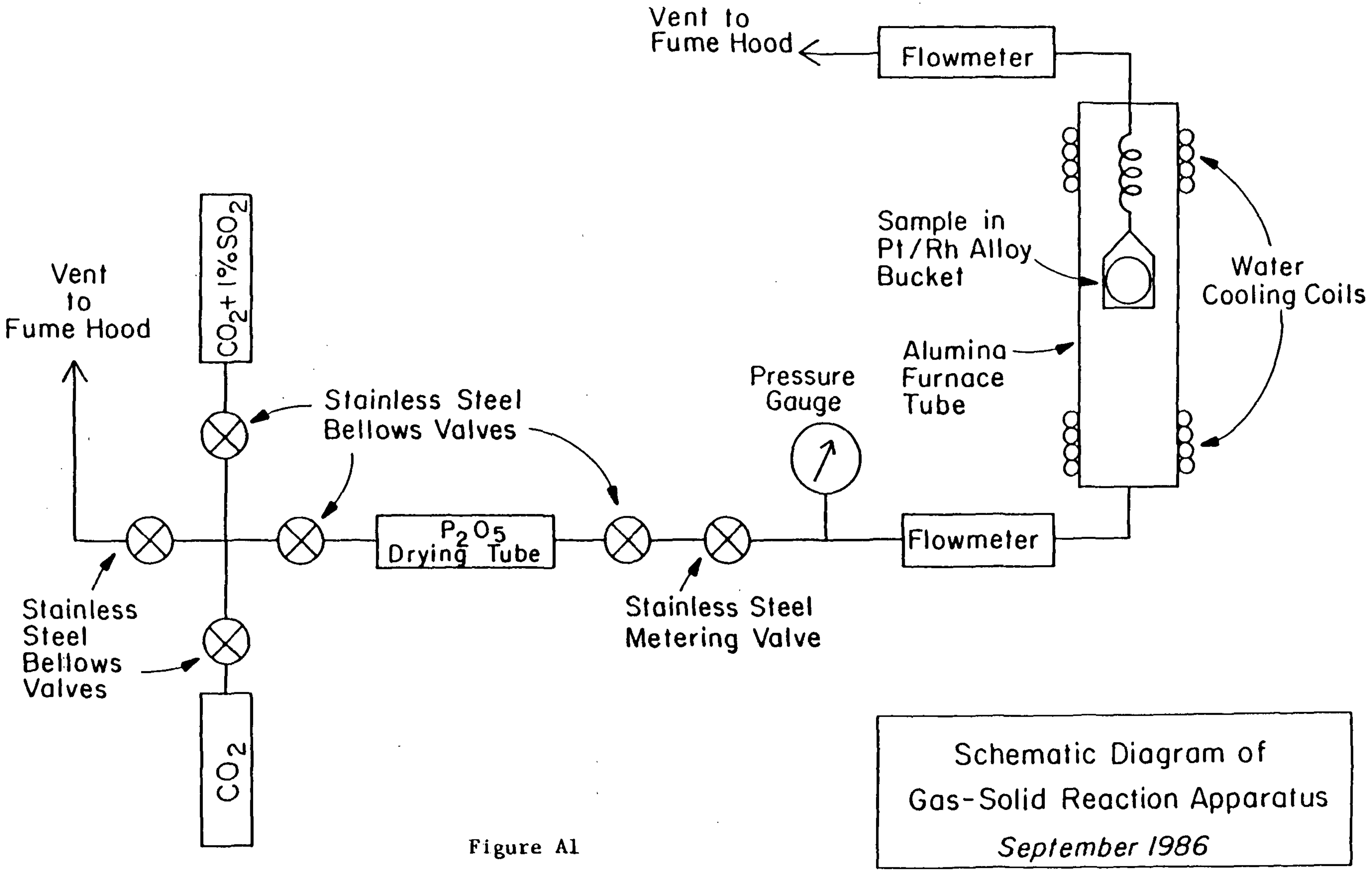
Notes to Table 1

[a] The estimated temperature uncertainty is ± 5°C.

[b] The number of SO_2 molecules reacted per cm^2 surface area per second. The rate is from weight gain measurements unless noted otherwise. The 1 σ uncertainties are also listed.

[c] The rate from ion chromatography analyses of SO_4^{2-} content of reacted sample.

[d] The rate from scanning electron microscope (SEM) measurements of anhydrite layer thickness and porosity.



Schematic Diagram of
Gas-Solid Reaction Apparatus
September 1986

Figure A1

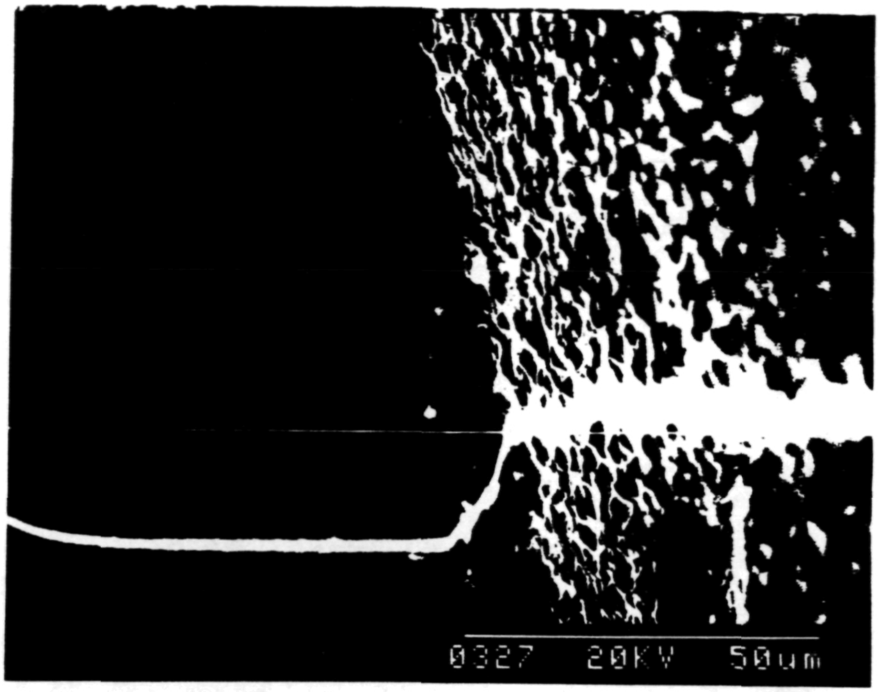


Figure A2. Scanning electron microscope (SEM) micrograph of the fracture surface of a reacted calcite ($CaCO_3$) crystal. The scale bar is 50 micrometers long. The horizontal white line on the micrograph shows the position of an X-ray line scan for the element sulfur. The way white line shows that sulfur X-rays are produced only at the reacted surface where grains of the mineral anhydrite ($CaSO_4$) are formed as a result of the gas-solid reaction.

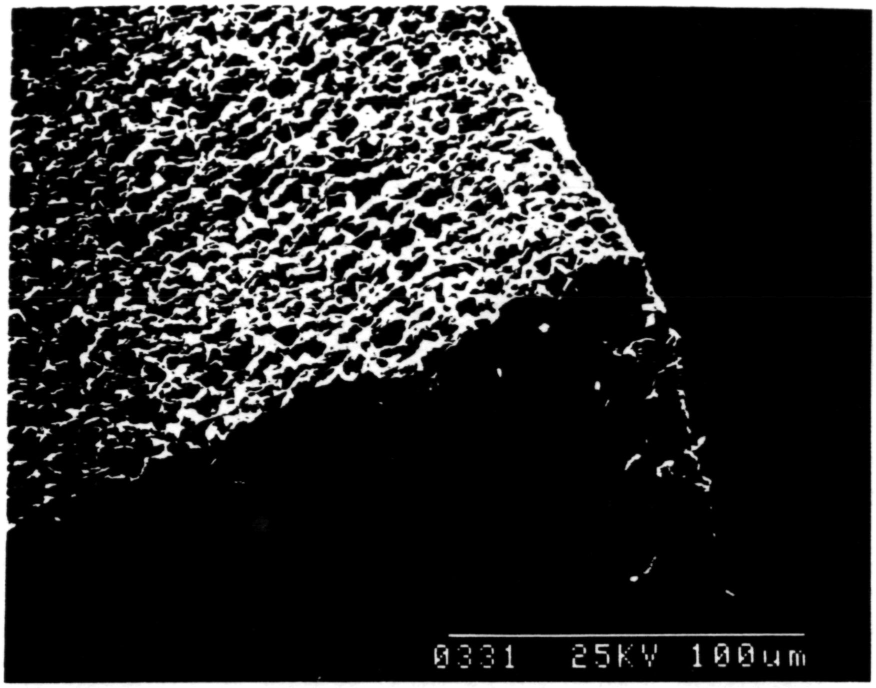


Figure A3. A SEM micrograph of the fracture surface of another reacted calcite crystal. The scale bar is 100 micrometers long. All external surfaces of the crystal are covered with a layer of anhydrite ($CaSO_4$) grains. This layer gradually becomes thicker as the gas-solid reaction continues.

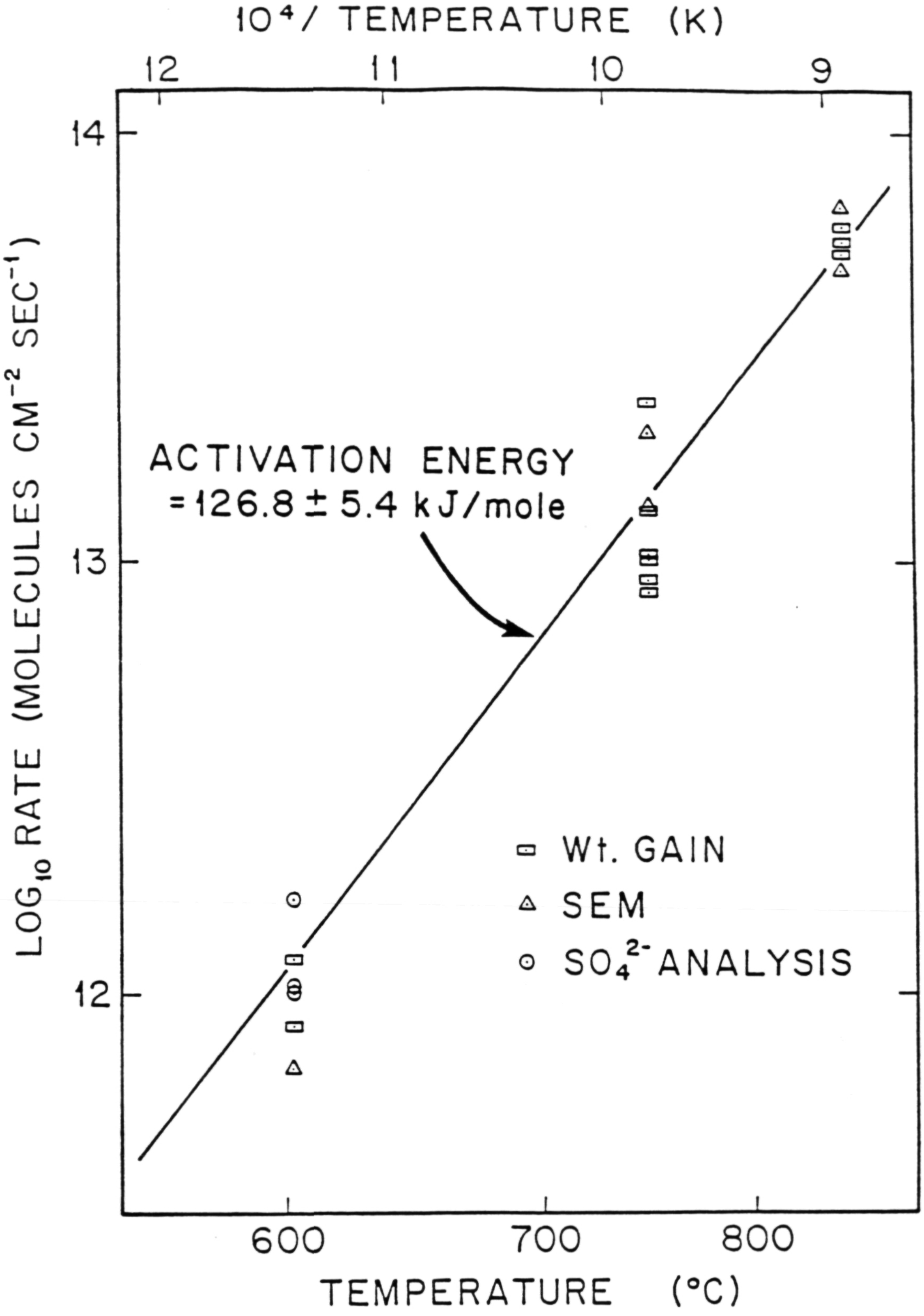


Figure A4. Arrhenius plot of rate data from Table A5 vs. 1/T. The line is a weighted linear least squares fit. Rates determined from independent methods (wt. gain, SEM, SO_4^{2-} analyses) for the same sample agree within the 1σ experimental uncertainties.

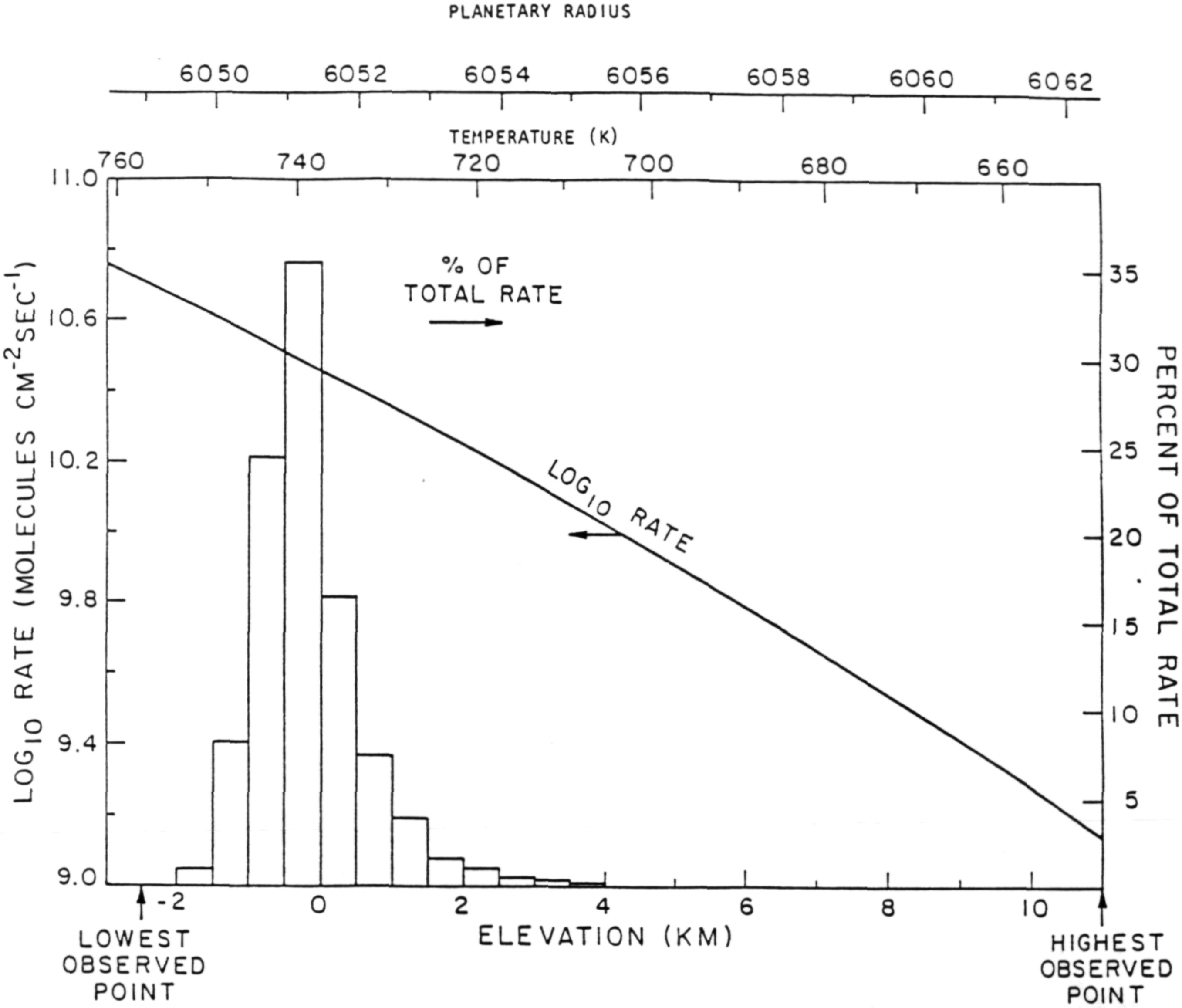


Figure A5. The rate of reaction (1) as a function of temperature and elevation on Venus. The bar graph shows the % of the total rate in each elevation increment. The solid line shows how the rate decreases with decreasing temperature. The global mean rate is $\sim 4.6 \times 10^{10}$ molecules cm^{-2} sec^{-1}

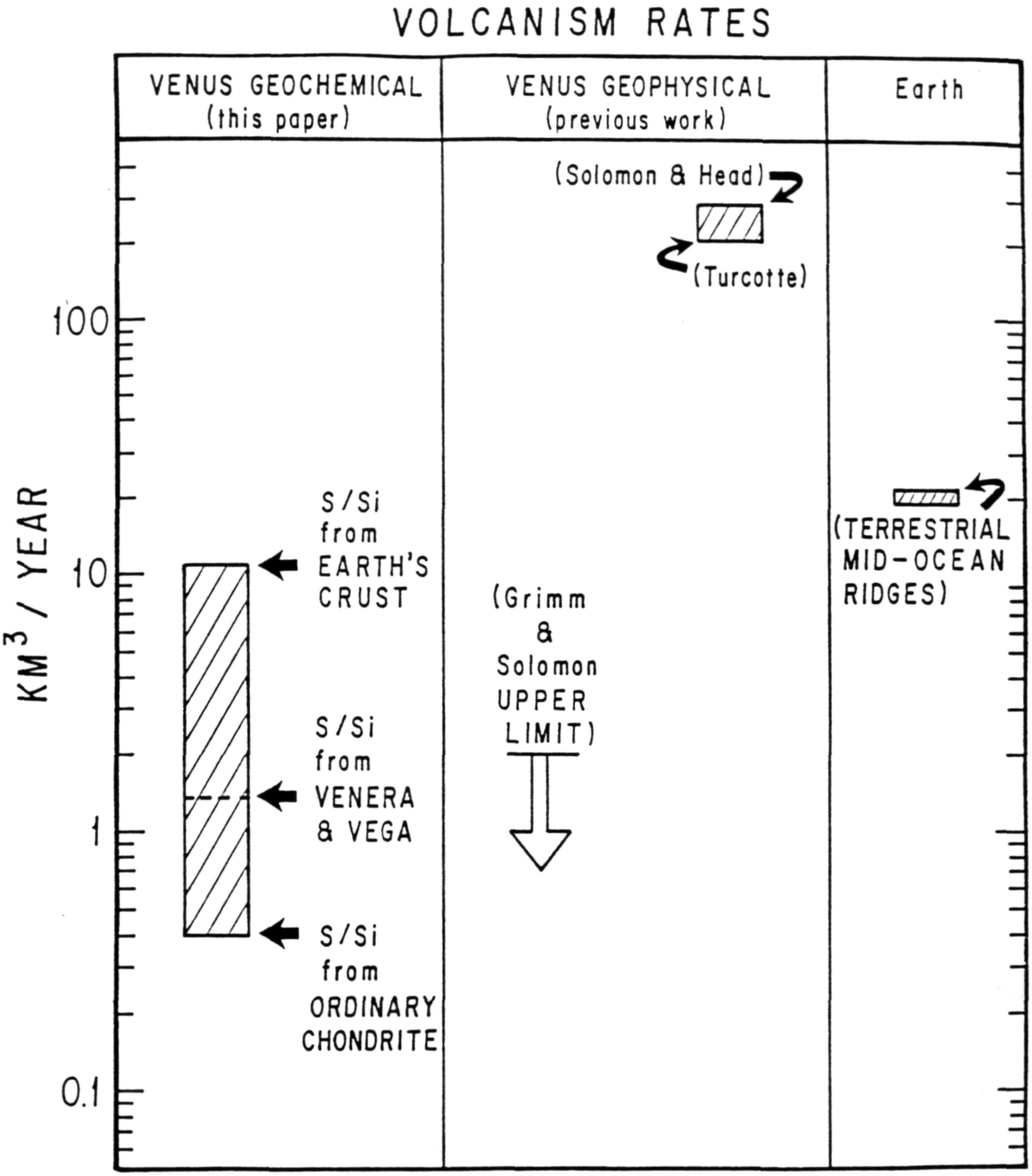


Figure A6. Independent geochemical and geophysical estimates of the rate of volcanism on Venus are compared to the terrestrial rate. Three plausible models for the S/Si ratio of erupted material on Venus yield rates of ~ 0.4 to ~ 11 km^3 yr^{-1}. Adopting the Venus surface S/Si ratio from Venera 13, 14 and Vega 2 analyses yields a rate of ~ 1 km^3 yr^{-1}, or about 20 times less than the rate of volcanism on Earth.

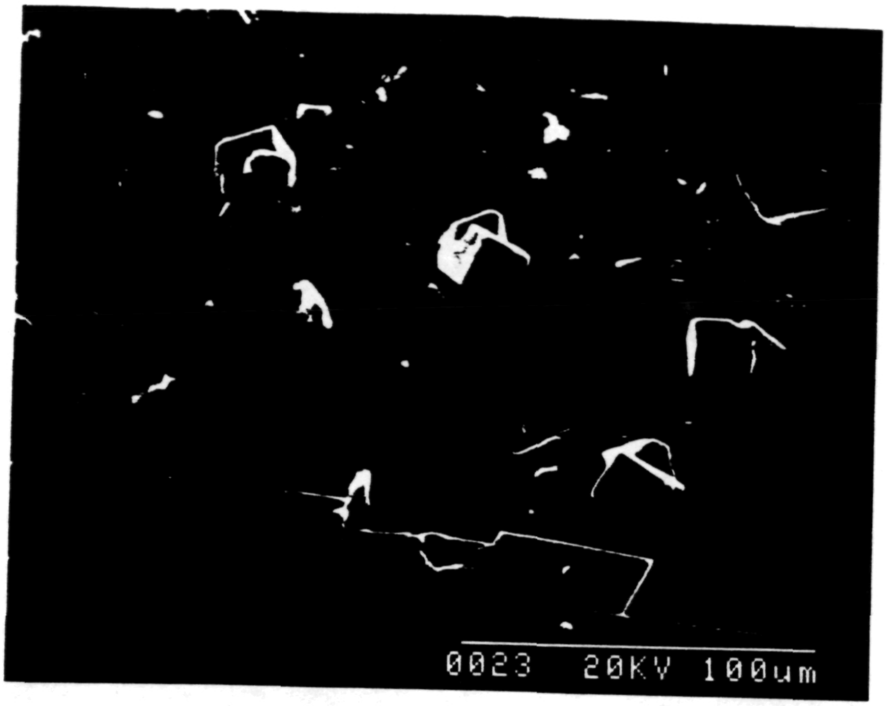


Figure A7. Scanning electron micrograph of pyrite (FeS_2) crystals on a dolomite $CaMg(CO_3)_2$ substrate. The scale bar is 100 microns long. See Figure A8 which shows pyrite crystals after high temperature reaction with CO_2 (gas).

Figure A8. Scanning electron micrograph of reacted pyrite (FeS_2) crystals heated at ~ 980°C for 3 hours. The scale bar is 100 microns long. The *"fluffy"* particles are the reacted pyrite crystals which have lost all sulfur and have been oxidized by the CO_2 atmosphere in the furnace. Compare to the unreacted crystals in Figure A7.

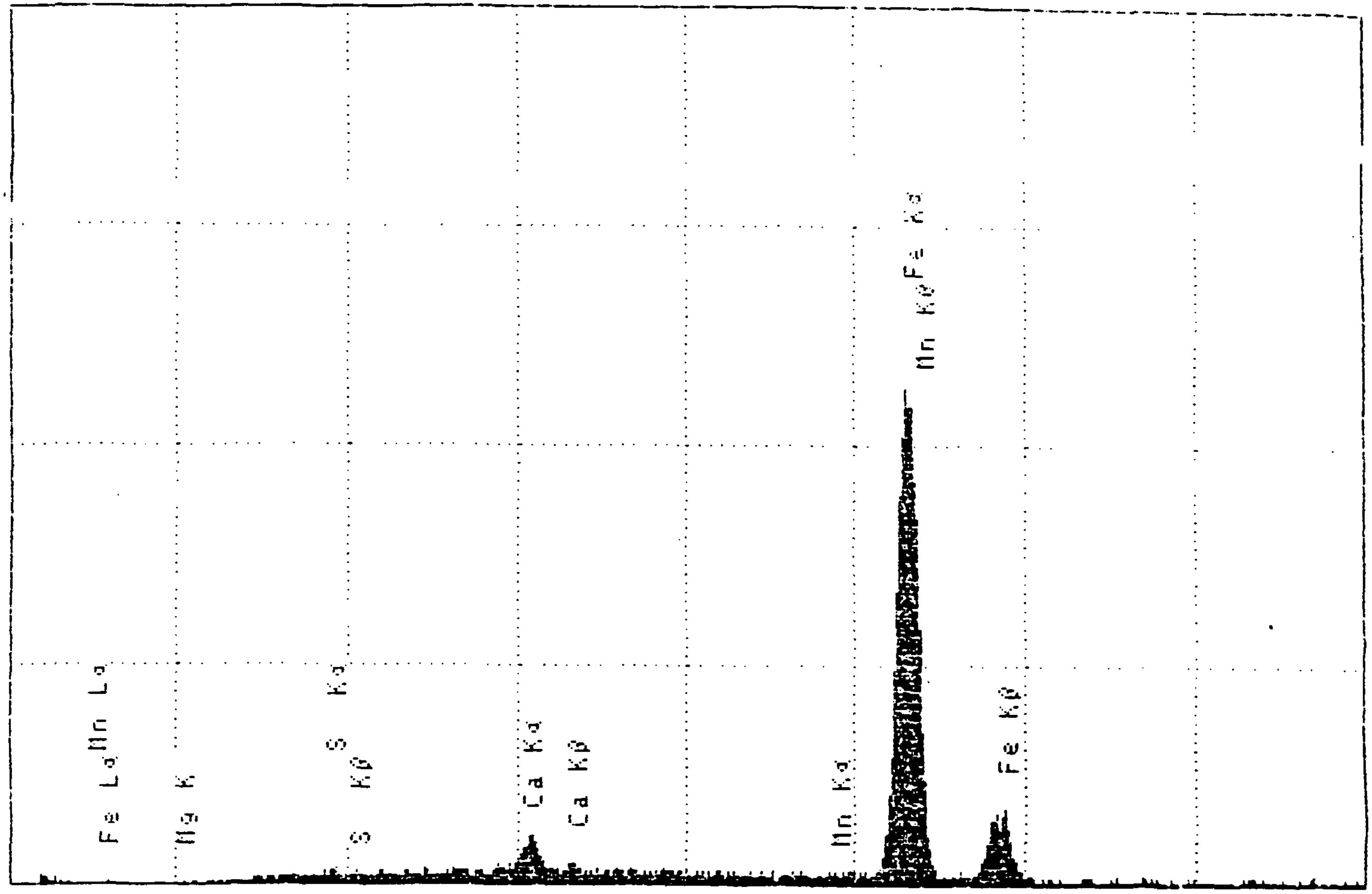


Figure A9. Chemical analysis of the reacted pyrite crystals in Figure A8. The analysis is done by energy dispersive spectroscopy on the scanning electron microscope (EDS/SEM). Peak intensities are on the vertical axis (1000 counts full scale) and peak energies are on the horizontal axis (0-10 Kev). Note that the reacted pyrite crystals have lost all sulfur and are now *Fe* oxide. Only *Fe* peaks from the reacted pyrite and *Ca* and *Mg* contamination from the surrounding dolomite (partially converted to $CaO + MgO$) show up because the oxygen and carbon peaks cannot be detected by EDS/SEM.